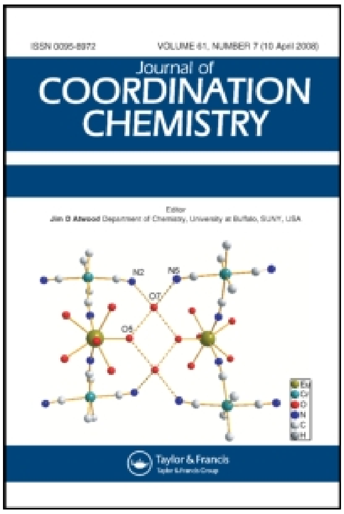

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Synthesis, crystal structure and properties of a novel copper(II) complex with tripod ligand *tris*(1H-benzimidazol- 2-ylmethyl)amine

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Synthesis, crystal structure and properties of a novel copper(II) complex with tripod ligand *tris*(1H-benzimidazol-2-ylmethyl)amine

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A five-coordinate copper complex with the tripod ligand *tris*(1H-benzimidazol-2-ylmethyl) amine (ntb), of composition $[Cu(ntb)(H_2O)] (C1O_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$ ($C_5H_4N_2O_3 = $ 4-nitro-pyridine-*N*-oxide), was synthesized and characterized by means of elemental analyses, electrical conductivities, thermal analyses, IR, and U.V. The crystal structure of the copper complex has been determined by single-crystal X-ray diffraction, and shows that the Cu^{II} is bonded to a *tris*(1H-benzimidazol-2-ylmethyl)amine (ntb) ligand and a water molecule through four N atoms and one O atom, giving a distorted trigonal–bipyramidal coordination geometry with approximate C_3 molecular symmetry. Cyclic voltammograms of the copper complex indicate a quasi-reversible Cu^{+2}/Cu^{+} couple. Electron spin resonance data confirm a trigonal-bipyramidal structure and with $g_2 < g_\xi$ and a very small value of A_2 ($20 \times 10^{-4}\,cm^{-1}$).

Keywords: *tris*(1H-Benzimidazol-2-ylmethyl)amine; Copper complex; Crystal structure

1. Introduction

Model systems that mimic the active sites of metalloenzymes are important not only for the understanding of enzyme mechanisms, but also for the development of small molecular weight biomimetic catalysts. Histidine imidazole plays an important role in the coordination of copper at the active sites of numerous copper proteins [1, 2]. For example, superoxide dismutases (SOD), which are contained in microbes, plants and animals, protects cells against oxygen toxicity, because these enzymes catalyze the conversion of superoxide (O_2^-) to hydrogen peroxide and dioxygen via redox-active metals [3, 4]. Tripodal ligands have long been used in both copper coordination and bioinorganic chemistry, typically tripyridylalkylamine and triazacyclononane tripodal ligands [5–7]. The tetradentate tripodal ligand, *tris*(2-benzimidazolylmethyl)amine (ntb) (figure 1), is similar to the histidine imidazole in coordination [8]. Since the three arms of this type of ligand can each rotate freely around an N(apical)–C bond, multicomponent complexes or

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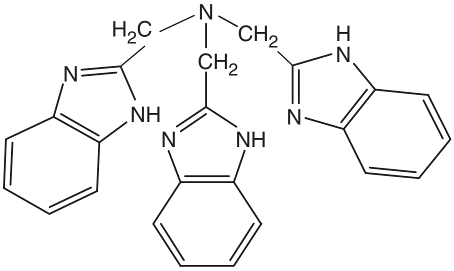

Figure 1. Structure of ntb.

coordination polymeric networks may be expected to form the assembly of this ligand by metal ions of low coordination number. Reports on the synthesis and spectroscopic characterization of copper(II) complexes with ntb have appeared in the literature [9–12]. In this article, we have prepared and investigated the properties and structure of the copper(II) complex with ntb and water as an exogenous ligand. The crystal structure data of $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$, obtained through single-crystal X-ray diffraction, reveal conclusively the bonding specificity and the coordination position of the copper complex in an effort to understand the coordination behavior of such ligands and the factors influencing the crystal packing modes. The copper(II) in the complex adopts a distorted trigonal–bipyramidal coordination geometry with the N_4O ligand donor set.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were reagent grade and used without further purification. C, H and N contents were determined using a Carlo Erba 1106 elemental analyzer. Metal content was determined by EDTA titration. Thermal studies of the complex were made in the 25–800°C range using a ZRY-2P thermal analyzer with a heating rate of $10^\circ C\,min^{-1}$. IR spectra were recorded in the 4000–400 cm^{-1} region with a Nicolet FI-IR Avatar 360 spectrometer using KBr pellets. Electronic spectra were taken on a TU-Visible spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using $10^{-3}\,mol\,L^{-1}$ solution in DMF at room temperature. ^1H NMR spectra were recorded on a Bruker AM200A NMR spectrometer with TMS as internal standard and DMSO-d_6 as solvent. Electrochemical measurements were performed on a LK98APLUS electrochemical analyzer under nitrogen atmosphere at 283 K. A glassy carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel electode (SCE) reference electrode were used in the three-electode measurements. The electroactive component was at $1.0 \times 10^{-3}\,mol\,dm^{-3}$ concentration with tetrabutylammonium perchlorate (TBAP) ($0.1\,mol\,dm^{-3}$) used as the supporting electrolyte in DMF. The EPR spectra were recorded on a Bruker 200D spectrometer with the X-band.

2.2. *Preparation of* tris*(2-benzimidazolylmethyl)amine (ntb) and copper complex*

tris(2-Benzimidazolylmethyl)amine (ntb) was synthesized by the literature method [13]. Yield: 19.5 g (60%); m.p.: 274–275°C (m.p.: 271°C in the literature [13]). The infrared spectra and ^{1}H NMR spectra of ntb were consistent with the literature [13].

2.2.1. $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$. To a stirred solution of ntb (0.4075 g, 1 mmol) in hot MeOH (20 cm^3) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.3704 g, 1 mmol), followed by a solution of 4-nitropyridine-*N*-oxide (0.1401 g, 1 mmol) in MeOH (5 cm^3). The resulting clear blue solution was stirred for 8 h and then allowed to stand at room temperature. Blue-green crystals suitable for X-ray diffraction studies were obtained after two weeks. Yield, 0.437 g (51%). Anal. Found: C, 40.95; H, 3.41; N, 14.63; Cu, 7.40. Calcd for $C_{29}H_{29}Cl_2CuN_9O_{13}$ (MW 846.05): C, 41.17; H, 3.43; N, 14.89; Cu, 7.51%. A_M(DMF, 297 K): 139 S cm^2 mol^{-1}.

2.3. *X-ray structure determination of $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$*

All data were obtained using a Bruker Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.071073 nm) at 293 K. Data reduction and cell refinement were performed using SMART and SAINT programs [14]. The absorption corrections were carried out by the empirical method. The structure was solved by direct methods (Bruker Shelxtl) using all unique data [15]. The non-H atoms in the structure were subjected to anisotropic refinement. Hydrogen atoms were located geometrically and treated with the riding model. The crystal data and experimental parameters relevant to the structure determination are listed in table 1 and the final positional and thermal parameters are available as supplementary material.

3. Results and discussion

The copper complex is soluble in EtOH and MeOH and easily soluble in DMF and DMSO, but insoluble in water, benzene, petroleum ether, trichloromethane etc. Elemental analysis shows the composition $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$. A comparsion of molar conductance value with those previously reported in the literature [16] shows 1 : 2 electrolytes of the complex in DMF.

TGA curve of the copper(II) complex shows that it undergoes endothermic dehydration. The initial mass loss within the 83–115°C range is attributed to elimination of the hydration H_2O molecules and a DTA curve indicates that the dehydration process is endothermic. The second mass loss, 160–193°C, is due to loss of 4-nitropyridine-*N*-oxide. The decomposition of the complex starts at 269°C and is completed at ca 610°C, yielding CuO as the final product.

3.1. *Crystal structure of $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$*

The molecular structure and crystal packing of the copper(II) complex are shown in figures 2 and 3; selected bond distances and angles are shown in table 2. The crystal structure consists of a discrete $[Cu(ntb)(H_2O)]^{2+}$ cation, two perchlorate anions,

Table 1. Crystal data and structure refinement for $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$.

Formula	$C_{29}H_{29}Cl_2CuN_9O_{13}$
Molecular weight(g mol^{-1})	846.05
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions(Å, °)	
a	11.986(3)
b	24.134(6)
c	14.226(3)
α	90.00
β	114.9130(10)
γ	90.00
V(Å^3)	3732.2(15)
Z	4
T(K)	293(2)
D(calculated)(g cm^{-3})	1.506
Absorption coefficient(mm^{-1})	0.802
F(000)	1732
Crystal size(mm^3)	0.2 × 0.2 × 0.3
θ range for data collection(°)	1.7–26.0
Index ranges	$-14 \le h \le 13$, $-29 \le k \le 29$, $-10 \le l \le 17$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7345[R(int) = 0.012]/0/496
Goodness-of-fit on F^2	1.005
Finial R_1 and wR_2 $[I > 2\sigma(I)]$	0.0446, 0.1272^a
R_1 and wR_2 indices(all data)	0.0586, 0.1310
Large diff. peak and hole (e Å^{-3})	0.35 and −0.34

$^a w = 1/[\sigma^2 F_0^2 + (0.07P)^2 + 1.99P]$, where $P = (F_0^2 + 2F_c^2)/3$.

a molecule of 4-nitropyridine-*N*-oxide and one water of crystallization, which is disordered over two sites with equal occupancies. The Cu^{II} atom is five-coordinate with a N_4O ligand set. The ntb ligand is a tetradentate N-donor, and an aqua O atom completes the coordination. The coordination geometry of the Cu^{II} atom is best described as distorted trigonal–bipyramid, with approximate molecular symmetry C_3. The coordination geometry around the Cu^{II} atoms appears to relieve the steric crowding. The equatorial plane is occupied by three N atoms of three benzimidazolyl groups, while the Cu^{II} atom protrudes towards O(1) and is 0.319(1) Å from the plane of atoms N(3)/N(5)/N(7). The axial positions are occupied by N(1) and O(1), with Cu–N(1) 2.127(3) Å, Zn–O(1) 1.957(3) Å and N(1)–Zn–O(1) is 176.52(10)°. The bond distance between the copper ion and the apical nitrogen atom 2.127(3) Å, which is about 0.094 Å longer than the bond distances between the copper ion and the trigonal basal nitrogen atoms (1.992–2.085 Å, average 2.033 Å). This significant elongation has been observed in copper complexes of tripodal tetradentate ligands with a benzimidazolylmethyl group [17]. The three benzimidazole ring arms of the ntb ligand form a cone-shaped cavity. The angles N(3)–Cu–N(5), N(5)–Cu–N(7) and N(3)–Cu–N(7) are 117.68 (11), 106.90(11) and 128.02(11)°, respectively. The N(1)–Cu–N(3) 80.78 (12), N(1)–Cu–N(5) 80.54(10) and N(1)–Cu–N(7), 81.57(10)° angles, which are all ca 10° less than the ideal 90°, are imposed by the geometry of the ntb ligand.

3.1.1. Crystal packing. The unsubstituted NH group and O(1) of the coordinated water molecule are potential hydrogen bond donors, which together with perchlorate

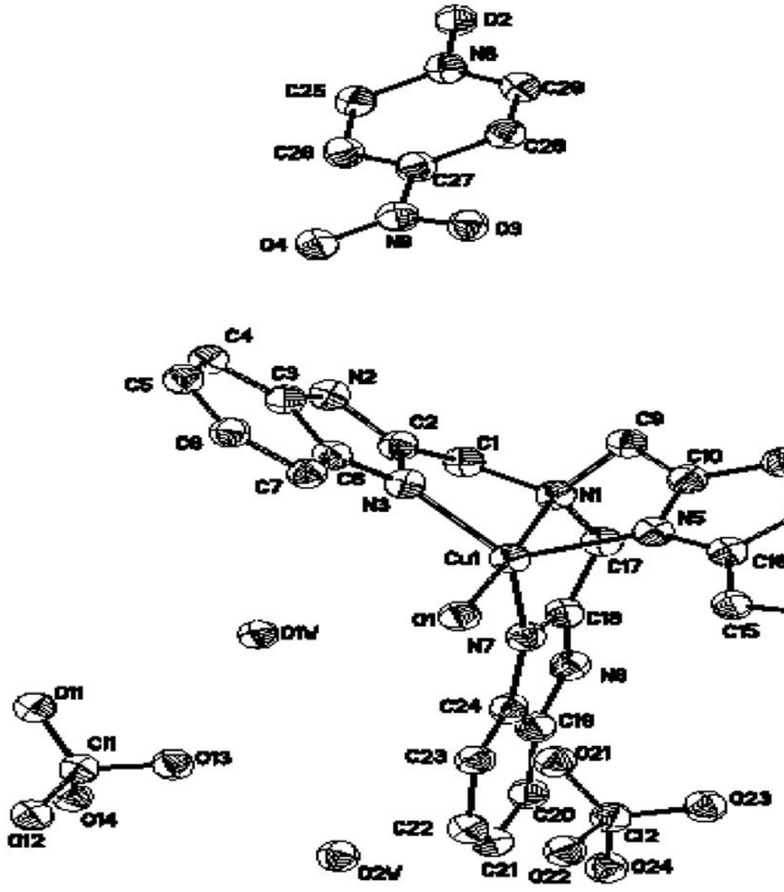

Figure 2. Molecular structure and atom numbering of $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$ with hydrogen atoms omitted for clarity.

and uncoordinated water, generate $N \cdots O$ and $O \cdots O$ hydrogen bonds as the dominant packing forces. In the crystal structure, intermolecular $O–H \cdots O$ and $N–H \cdots O$ hydrogen bonds, along with weak intermolecular $C–H \cdots O$ hydrogen bonds and a single significant $\pi \cdots \pi$ stacking interaction [where $Cg1 \cdots Cg1$ $(2-x, -y, 1-z) = 3.6833$ (3) Å ($Cg1$ is the centroid of ring atoms C(10)/N(4)/C(11)/C(16)/N(5)) and the perpendicular distance is 3.49 Å] connect cations, anions and solvent molecules into a three-dimensional network. The selected hydrogen bonds are listed in table 3.

3.2. *IR and electronic spectra*

The IR spectral data for the copper complex along with assignments are given in table 4. In the free ligand ntb, a strong band is found at ca $1440\,cm^{-1}$ together with a weak band at $1460\,cm^{-1}$. By analogy with the assigned bands of imidazole, the former is attributed to ν(C=N–C=C), while the latter is ν(C=N) [5, 18, 19]. They shift to higher frequency ca $10–30\,cm^{-1}$ in the complex, which implies direct coordination of all four

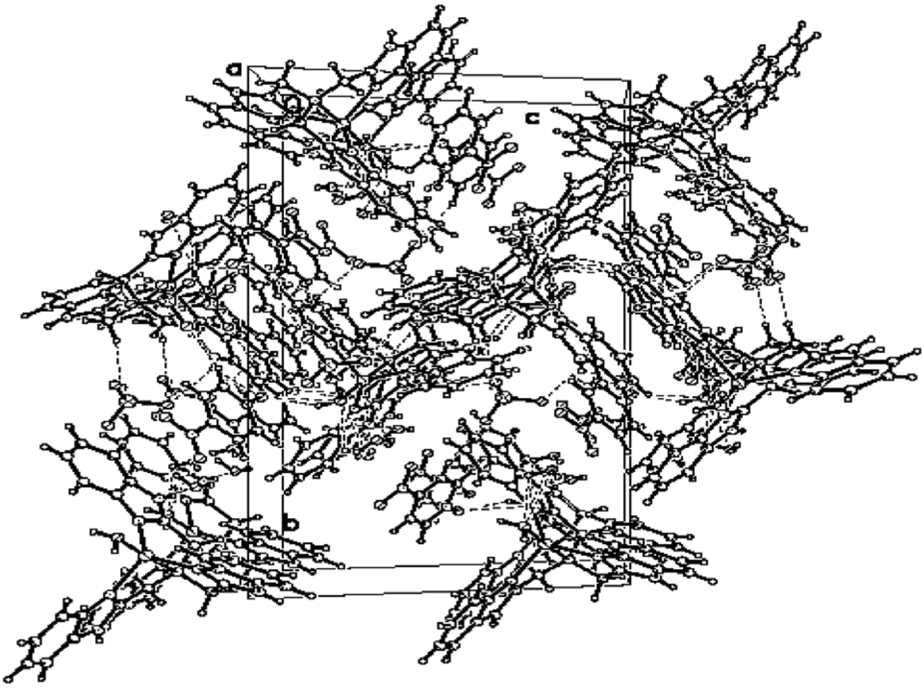

Figure 3. Packing structure along the *a* axis of $[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$.

Table 2. Slected bond distances(Å) and angles(°).

Cu–O(1)	1.957(3)	Cu–N(1)	2.127(3)
Cu–N(3)	1.992(3)	O(2)–N(8)	1.280(4)
Cu–N(5)	2.085(3)	N(9)–O(3)	1.222(4)
Cu–N(7)	2.022(3)	N(9)–O(4)	1.205(4)
O(1)–Cu–N(3)	97.92(14)	N(3)–Cu–N(1)	80.78(12)
O(1)–Cu–N(5)	102.72(10)	N(5)–Cu–N(1)	80.54(10)
O(1)–Cu–N(7)	98.53(10)	N(7)–Cu–N(1)	81.57(10)
N(3)–Cu–N(5)	117.68(11)	O(2)–N(8)–C(25)	118.9(3)
N(3)–Cu–N(7)	128.02(11)	O(2)–N(8)–C(29)	122.2(3)
N(5)–Cu–N(7)	106.90(11)	C(25)–N(8)–C(29)	119.0(4)
O(1)–Cu–N(1)	176.52(10)	C(1)–N(1)–Cu	106.2(2)
C(1)–N(1)–C(17)	110.1(3)	C(17)–N(1)–Cu	108.4(2)
C(1)–N(1)–C(9)	113.2(3)	C(9)–N(1)–Cu	106.79(19)
C(17)–N(1)–C(9)	111.8(2)		

imine nitrogen atoms to copper(II). This is the preferred nitrogen atom for coordination as found for other metal complexes with benzimidazoles [20]. Information regarding the possible bonding modes of the perchlorate may also be obtained from the IR spectra. The strong, fairly broad absorption band at $1119\,cm^{-1}$ indicates that the ionic perchlorate groups (Td) are present [21]. The bands of 4-picoline-*N*-oxide are unshifted, which supports the hypothesis that the 4-picoline-*N*-oxide is not coordinated with the central metal ion in the complex. This conclusion is confirmed by the crystal structure analysis.

Table 3. Selected hydrogen bonding distances(Å) and angles(°).

D–H···A	D–H	D···A	H···A	∠D–H···A
O1–H1C···O21	0.8500	3.230(4)	2.4400	156.00
O1–H1E···O2	0.8200	2.807(3)	2.1700	135.00
01W–H1WC···01	0.8500	2.733(5)	2.3400	108.00
N4–H4A···O2	0.8600	3.274(4)	2.5700	139.00
N4–H4A···O14	0.8600	3.159(4)	2.4800	136.00
N6–H6A···O24	0.8600	2.964(4)	2.1400	161.00
C1–H1A···O12	0.9700	3.353(5)	2.4900	147.00
C1–H1B···O24	0.9700	3.469(5)	2.5400	160.00
C17–H17B···O11	0.9700	3.265(4)	2.3800	152.00
C26–H26···O4	0.9300	2.704(5)	2.3800	100.00

Table 4. IR and UV spectral data for the Cu complex and their relative assignments.

	IR (cm^{-1})			UV-Vis [λ_{max} (nm)]		
Compound	ν(C=N)	ν(C=N–C=C)	$\nu(ClO_4^-)$	$n \rightarrow \pi^*$, $n \rightarrow \pi^*$	$d_{xz,yz} \rightarrow d_{z^2}$	$d_{xy} \rightarrow d_{z^2}$
ntb	1460 m	1440 s	–	284, 277	–	–
Cu complex	1483 m	1453 s	1117 bs	281, 274	775	896

b = broad; s = strong; m = medium.

A DMSO solution of ntb and the copper complex show, as expected, identical UV spectra. The UV bands of ntb (284, 277 nm) are only marginally blue shifted (3–4 nm) in the complex, clear evidence of C=N coordination to copper. Two absorption bands are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (imidazole). The copper complex exhibits two absorptions in the visible spectra ($\lambda = 775$, 896 nm). The higher-energy band is (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) transition, while the next lower energy transition is ($d_{xy} \rightarrow d_{x^2-y^2}$) [9]. This spectral pattern is typical of five-coordinate trigonal bipyramidal copper(II). Known trigonal bipyramidal systems, e.g. $[Cu(Me_6tren)X]^+$and $[Cu(tren)L]^{n+}$ (tren = $N(CH_2CH_2NH_2)_3$; $Me_6tren = N[CH_2CH_2N(CH_3)_2]_3$; X = Cl, Br, I, NO_3, ClO_4; L = OH, py, NH_2Ph, NCS, NH_3) exhibit very similar spectra [22, 23].

3.3. *Electrochemistry and EPR spectra*

The electrochemical properties of the copper complex have been studied by cyclic voltammetry (CV) in DMF. The voltammogram of the copper(II) complex shows only a single reduction peak (Cu^{2+}/Cu^+) at −0.20 V during the cathodic potential scan. During the return anodic potential scan, just after the reduction peak, an anodic peak is observed at −0.02 V. The separation between the cathodic and anodic peak potentials $\Delta\varepsilon_\rho$ ($\Delta E_p = E_{pa} - E_{pc}$) of 180 mV indicates a quasi-reversible redox process assignable to the Cu(II)/Cu(I) couple and $E_{1/2}$ [$(E_{pa} + E_{pc})/2$] is equal to −0.11 V [24, 25]. The neutral uncomplexed ligand ntb is not electroactive over the range −1.2–+1.2 V.

The X-band EPR spectrum was measured in single crystal at 285 K (figure 4). The fact that $g\| = g_{zz}$ and $g\perp = g_{xx} = g_{yy}$ shows that the spectral features are of axial symmetry. Copper complexes of tren, Me_6tren, Et_6tren which have trigonal-bipyramidal structures have $g\| < g\perp$ and $A\|$ in the range ~65–100 ($10^{-4}\,cm^{-1}$) [9, 22, 23].

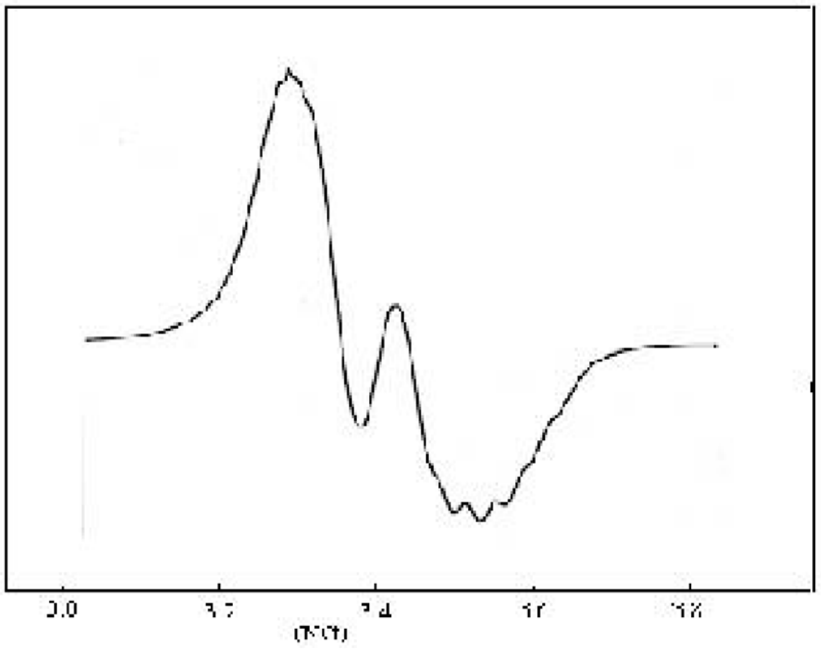

Figure 4. X-band EPR Spectrum of the copper complexe at 285 K in single crystal. Spectrometer conditions: microwave frequency, 9.65 GHz; microwave power, 10 mW; gain, 4.0 × l0^4; mid-range, 3181 G; scan range, 2000 G; time constant, 0.5 s; scan time, 200 s.

Table 5. EPR spectral of the copper complex in single crystal at 285 K.

Complex	$g\|$	$g\perp$	$g^{a}_{av.}$	$\alpha\| (\times 10^{-4})$	$A\perp (\times 10^{-4})$
$[Cu(ntb)(H_2O)](ClO_4)_2 \cdot C_5H_4N_2O_3 \cdot H_2O$	2.047	2.230	2.169	20 cm^{-1}	45 cm^{-1}

[a] $g_{av.} = (g\| + 2g\perp)/3$.

Spin–Hamiltonian parameters for the copper complex, table 5, show $A\|$ is low and $g\|$ is greater than g_e. Eleven system of this type is interpreted in terms of a d_{z^2} ground state in a trigonal–bipyramid but the large value of $g\|$ implies the mixing of d_{xy} and $d_{x^2-y^2}$ orbitals into the groung state via vibronic coupling. Because $g\| < g\perp$ and the low $A\|$ value, the structure of the copper complex is best described as distorted trigonal–bipyramid.

Supporting information available

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

References

[1] C.T. Branden. *The Enzymes*, 3rd Edn, pp. 104–178, Academic Press, New York (1975).
[2] K.A. Thomas, B.H. Rubin, C.J. Bier, J.S. Richardson, D.C. Richardson. *Proc. Natl. Acad. Sci.*, **72**, 134 (1975).
[3] J.S. Valentine, D.M. Defreitas. *J. Chem. Educ.*, **62**, 990 (1985).
[4] D.C. Richardson, K.A. Thomas, E.W. Silevrton, D.R. Davies. *J. Mol. Biol.*, **102**, 221 (1976).
[5] M. Schatz, M. Becker, F. Thaler, F. Hampel, S. Schindler, R.R. Jacobson, Z. Tyeklar, N.N. Nurthy, P. Ghosh, Q. Chen, J. Zubieta, K.D. Karlin. *Inorg. Chem.*, **40**, 2312 (2001).
[6] K. Jitsukawa, M. Harata, H. Arii, H. Sakurai, H. Masuda. *Inorg. Chim. Acta*, **324**, 108 (2001).
[7] Q.X. Li, W. Zhang, Q.H. Luo, Y.Z. Li, Z.L. Wang. *Trans. Met. Chem.*, **28**, 682 (2003).
[8] W.H. Zhou, Z.W. Miao, X.L. Liu, F.M. Miao, H.G. Wang, X.K. Yao. *Chinese J. Struct. Chem.*, **18**, 204 (1999).
[9] L.K. Thompson, B.S. Ramaswamy, R.D. Dawe. *Can. J. Chem.*, **56**, 1311 (1978).
[10] Y. Nakao, M. Onoda, T. Sakurai, A. Nakahara, I. Kinoshita, S. Ooi. *Inorg. Chim. Acta*, **151**, 55 (1988).
[11] H.N. Pandey, Y.S. Sharma, P. Mathur. *Polyhedron*, **11**, 2631 (1992).
[12] Z.X. Su, Y.Q. Wan, H.L. Wu. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **35**, 553 (2005).
[13] L.K. Thompson, B.S. Ramaswamy, E.A. Seymour. *Can. J. Chem.*, **55**, 878 (1977).
[14] Bruker. *Smart Saint and Sadabs*, Bruker Axs, Inc., Madison, Wisconsin, USA (2000).
[15] G.M. Sheldrick. *SHELXTL*, Siemmens Analytical X-Ray Instruments, Inc., Madison, Wisconsin, USA (1996).
[16] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[17] J. Sletten, H. Grove. *Acta Chem. Scand.*, **51**, 822 (1997).
[18] C.Y. Su, B.S. Kang, C.X. Du, Q.C. Yang, T.C.W. Mak. *Inorg. Chem.*, **39**, 4843 (2000).
[19] T.J. Lane, I. Nakagawa, J.L. Walter, A.J. Kandathil. *Inorg. Chem.*, **1**, 267 (1962).
[20] M. McKee, M. Zvagulis, C.A. Reed. *Inorg. Chem.*, **24**, 2914 (1985).
[21] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, pp. 200–320, John Wiley and Sons, New York (1978).
[22] M. Ciamolini, N. Nardi. *Inorg. Chem.*, **5**, 41 (1966).
[23] G. Albertin, E. Bordignon, A.A. Orio. *Inorg. Chem.*, **14**, 1411 (1975).
[24] A.W. Addison, H.M.J. Hendriks, J. Reedije, L.K. Thompson. *Inorg. Chem.*, **20**, 103 (1981).
[25] K. Jitsukawa, M. Harata, H. Arii, H. Sakurai, H. Masuda. *Inorg. Chim. Acta*, **324**, 108 (2001).